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Syndiotactic-Specific Polymerization of 4-Methyl-1,3-pentadiene: Insertion on a Mt−CH$_3$ Bond

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Polymerization of 4-methyl-1,3-pentadiene (4-MPD) to 1,2 syndiotactic polymer is promoted by many homogeneous catalytic systems consisting of titanium or zirconium compounds, soluble in aromatic hydrocarbons, and methylaluminoxane (MAO).[1−3]

The same catalytic systems promote polymerization of ethylene and α-olefins,[4] of styrene and substituted styrenes,[5] and of conjugated diolefins.[2,3] Conjugated diolefins and styrenes can also be copolymerized in the presence of the title catalysts, affording statistical copolymers.[6,7]

It is worth noting (see Table 1) that the behavior of 4-MPD is closer to that of styrene than to that of, *e.g.*, 1,3-butadiene or isoprene, that produces 1−4 cis polymers.[2]

Table 1.[a] **Homopolymerizations of Butadiene, Styrene, Isoprene, and 4-Methyl-1,3-pentadiene in the Presence of CpTiCl$_3$−MAO**

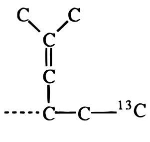
run	monomer	[monomer], mol/L	time, min	yield mg	main structure
1[b]	butadiene	1.72	4	96	1−4 cis
2[b]	styrene	1.68	15	190	1−2 syndiotactic
3[b]	isoprene	1.72	1000	60	1−4 cis
4[c]	4-MPD	1.33	3	45	1−2 syndiotactic

[a] This table was reprinted from ref 2 with permission of the authors. [b] These runs were performed in the presence of 1.0×10^{-5} mol of CpTiCl$_3$ and 1.0×10^{-2} mol of MAO, using 13 mL of toluene as solvent at 18 °C. [c] This run was performed in the presence of 2.5×10^{-8} mol of CpTiCl$_3$ and 3.5×10^{-3} mol of MAO in 13 mL of toluene, at 18 °C.

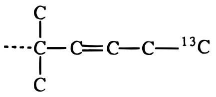
In this paper we report some information concerning the initiation step for polymerization of 4-methyl-1,3-pentadiene in the presence of a typical homogeneous catalyst prepared by reaction of CpTiCl$_3$−MAO and Al(^{13}CH$_3$)$_3$ (Cp = cyclopentadienyl).

The presence of Al(^{13}CH$_3$)$_3$ among the constituents of the catalyst is not needed for promoting polymerization, but it is required in order to observe, by ^{13}C NMR analysis of the resulting polymer, the structure of the end groups arising from the initiation step when the growing of a polymer chain begins by insertion of the first molecule of monomer into the Ti−^{13}CH$_3$ bond. As a matter of fact, the organometallic cations (CpTiR)$^+$ (R = hydrocarbyl) that promote the polyinsertion[8,9] can exchange the R ligand with Al(^{13}CH$_3$)$_3$ (chain termination via chain transfer to metal alkyls).

Figure 1 is the ^{13}C NMR spectrum of a sample of poly(4-methyl-1,3-pentadiene) obtained at 18 °C in the presence of the just-mentioned catalyst. Comparison with the spectra reported in the literature[1] shows that the polymer is highly syndiotactic and highly regioregular. Two additional sharp resonances in 7/3 intensity ratio are observed at 11.9_0 and 13.9_1 ppm (TMS scale). Comparison with the spectrum of a polymer prepared without addition of Al(^{13}CH$_3$)$_3$ demonstrates that these resonances are due to the enriched methyls and the chemical shifts are those expected for the following end groups (see the Experimental Section):

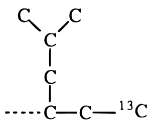


(t$_1$)

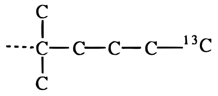


(t$_2$)

The assignment of these end groups has been confirmed by ^{13}C NMR analysis of the same polymer after catalytic hydrogenation (syndiotactic poly(4-methyl-1-pentene); see the experimental part) and by observation of two resonances at 8.6_6 and 12.0_0 ppm (HMDS scale) diagnostic of the enriched methyls of the saturated end groups:

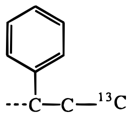


(t$_1$')



(t$_2$')

End group t$_1$ is not surprising at all, since a similar experiment performed while polymerizing styrene instead of 4-methyl-1,3-pentadiene showed exclusively the corresponding end group:



(secondary insertion of the monomer).[10] The presence of a considerable number of end groups t$_2$ was unexpected in view of the fact that we did not detect any 1,4 unit, within the limit of our experimental accuracy along the polymer chains. Thus, the initiation step involves a very regiospecific attack by the methyl to C$_1$ of the incoming monomer, according to Scheme 1, where η^3 coordination of the chain is assumed. The next incoming monomer can be attacked either by carbon labeled a or by that labeled b in Scheme 1, producing the observed end groups. The subsequently incoming monomers (propagation steps) are always attacked at C$_1$ by carbon labeled c in Scheme 2. At the present, the different chemioselectivity observed for initiation (Scheme 1) and for chain propagation (Scheme 2) cannot be unequivocally explained. In addition, there is not any clear-cut evidence of π allyl rather than σ bonding of the growing chain to Ti. However when comparing Schemes 1 and 2, one could speculate that the dimethylvinyl side substituent of the monomer unit, next to that coordinated to Ti, could play a role in determining the attack to the incoming unit. Possibly, backbiting coordination to the coordinative unsaturated Ti of the catalytically active cation of this group could favor the attack by carbon c in comparison with Scheme 1 where the main attack is also by carbon b, but attack by carbon a is also significant. One could also speculate that backbiting could shift coordination of the growing chain from π allyl to σ allyl, justifying the exceptionally high polymerization rate of 4-MPD in comparison with other conjugated diolefins.[11] It is worthwhile to mention that

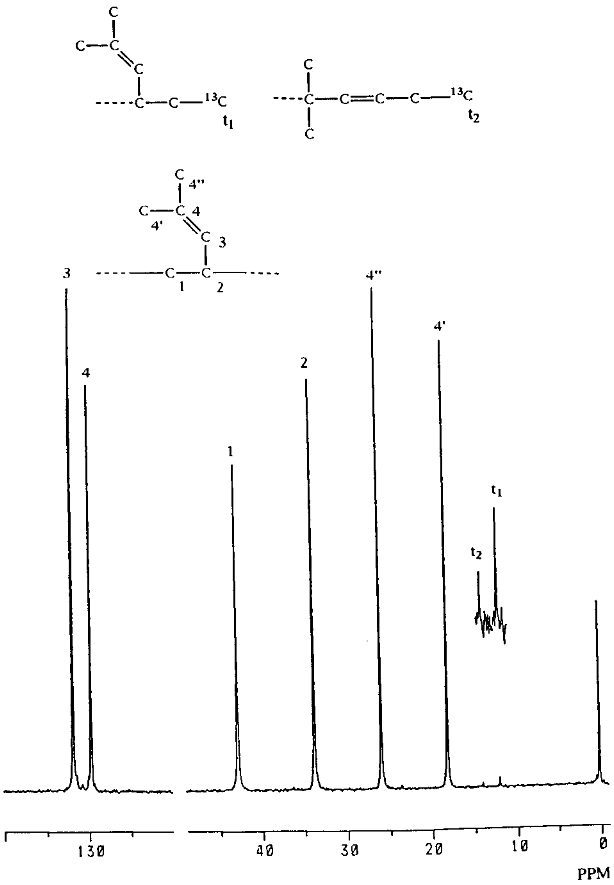
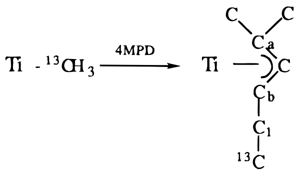
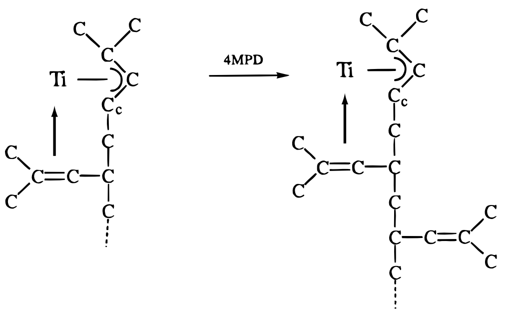


Figure 1. ^{13}C NMR spectrum of sample 1. TMS scale.

Scheme 1



Scheme 2



a similar backbiting of the chain has been observed for dimerization of butadiene to 3-methylhepta-1,4,6-triene by Giannini and co-workers.[12]

Experimental Section

Toluene was refluxed 48 h over Na benzophenone and distilled before use. 4-MPD was purified by distillation in the presence of $Al(C_2H_5)_3$.

$CpTiCl_3$, MAO, and $Al(^{13}CH_3)_3$ were synthesized according to published procedure.[9,13,14]

Sample 1 was prepared in a 50 mL glass flask under a nitrogen atmosphere by introducing sequentially 5 mL of toluene, 2 mL of 4-MPD, and, after thermostating at −80 °C, 1.0 mL of 0.3 M (50% enriched) $Al(^{13}CH_3)_3$. The temperature of the mixture was increased to 18 °C in 0.5 h, and then the reaction was started by introducing 1×10^{-5} mol of $CpTiCl_3$ dissolved in 1 mL of toluene.

Sample 2 was prepared following the same procedure of sample 1, but using $Al(CH_3)_3$ instead of $Al(^{13}CH_3)_3$.

Polymerizations were stopped after 4 h by injecting acidified ethanol; the polymer was coagulated in alcohol, recovered by filtration, washed twice with ethanol, and dried in vacuo.

Yields: 120 mg for run 1 and 150 mg for run 2.

Hydrogenations of samples 1 and 2 were carried out by dissolving 80 mg of the polymer in 50 mL of decalin in a 150 mL shaking autoclave, submersed in an oil bath thermostated at 130 °C in the presence of 100 mg of 10% palladium supported on charcoal and 30 bar of hydrogen. After 24 h, the mixture, filtered over silica gel at 130 °C, was poured into ethanol. The polymer was recovered by filtration and dried in vacuo.

The ^{13}C NMR spectra were recorded on an AM 250 Bruker spectrometer operating in the FT mode at 62.89 MHz.

Samples 1 and 2 were dissolved in $CDCl_3$ containing tetramethylsilane (TMS) as an internal chemical shift reference. The hydrogenated samples were dissolved in $C_2D_2Cl_4$, and the spectra were recorded at 120 °C. Hexamethyldisiloxane (HMDS) was used as an internal reference.

The assignments of the resonances of the enriched methyl of the different end groups are according to a computer program for the prediction of ^{13}C-NMR spectra based on an open set of additivity rules.[15]

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